Quantitative comparison and further interpretation must await direct optical studies. This series of compounds is the first reported system in which incremental distance effects on electron-transfer rates have been observed in rigid models of the photosynthetic primary process. Theoretical studies aimed at determining the role of the bicyclooctane spacer are under way.

Acknowledgment. We are grateful to the National Science Foundation (CHE-8305790 and DMR-8107494) and to the Southern California Regional NMR Facility (NSF Grant 7916324) for generous support of this research.

---

(14) From differential pulse voltammetry, the oxidation potential E_0 of the free base porphyrin **3a** in CH_2Cl_2 (0.1 M TBAP) is +0.79 V vs. SSCE. The redox potential for the reduction of the quinone **3a** is −0.64 V vs. SSCE. From the singlet excitation energy (W^*) of 1.98 eV we calculate the driving force for the forward electron transfer to be $\Delta G \sim 0.55$ V from $-E_0(P/P^+) + W^*(P/P^*) + E_0(Q/Q^-)$. For ZnPLQ **3b**, $E_0(P/P^+) = +0.54$ V, $E_0(Q/Q^-) = -0.64$ V vs. SSCE, $W^* = 2.15$ eV and $\Delta G = +0.97$ V. We thank Professor F. Anson and Dr. M. Sharp for generous assistance in carrying out the electrochemical measurements.

Silicoaluminophosphate Molecular Sieves: Another New Class of Microporous Crystalline Inorganic Solids

Brent M. Lok,* Celeste A. Messina, R. Lyle Patton,
Richard T. Gajek, Thomas R. Cannan, and
Edith M. Flanigen

Union Carbide Corporation
Tarrytown Technical Center
Tarrytown, New York 10591

Received June 29, 1984

The well-known classes of molecular sieves comprise the aluminosilicate zeolites,[1] including phosphorus-substituted aluminosilicates,[2,3] the microporous silica polymorphs,[4] and the recently discovered aluminophosphate molecular sieves.[5] Now another novel class of crystalline microporous framework oxide molecular sieves, the silicoaluminophosphates, has been synthesized.[6] These new materials have properties both of zeolites and of aluminophosphates yet are unique in many ways. They should find uses as adsorbents for separation and purification of molecular species, as catalysts or catalyst supports, and as ion-exchange agents.

The new family of silicoaluminophosphate materials (SAPO-n)[7] exhibits structural diversity with some 13 three-dimensional microporous framework structures known to date. These include novel structures, SAPO-40, SAPO-41, and SAPO-44, structures topologically related to the zeolites, chabazite (SAPO-34), levynite (SAPO-35), faujasite (SAPO-37), and A (SAPO-42), structures topologically related to the novel structure types found in the aluminophosphates, including SAPO-5, SAPO-11, SAPO-16, and SAPO-31,[5] and topological relatives of structures found in both zeolites and aluminophosphates, erionite (SAPO-17) and sodalite (SAPO-20).

Members of the new class of molecular sieves are synthesized hydrothermally, as are the synthetic zeolites and aluminophosphates. The materials crystallize at 100–200 °C from reactive mixtures containing organic amine or quaternary ammonium templates (R) which are retained within the products. Reactive alumina, phosphate, and silica sources, such as hydrated aluminum oxide, phosphoric acid, and silica sol, were used in synthesis. The species R appears essential to the synthesis of these novel phases since in its absence amorphous or dense crystalline materials form.

The silicoaluminophosphates encompass a wide compositional range of $0\text{–}0.3R\cdot(Si_xAl_yP_z)O_2$ in the anhydrous form, where x, y, and z represent the mole fractions of silicon, aluminum, and phosphorus and range from 0.01 to 0.98, 0.01 to 0.60, and 0.01 to 0.52, respectively, with $x + y + z = 1$.

Table I lists the SAPO species, the templates used in their synthesis, and the structure type determined from X-ray powder diffraction patterns. The template–structure relationships observed in the aluminophosphate molecular sieves[5,9] are again found here. SAPO-17 and SAPO-20 are formed in the presence of the templates quinuclidine and tetramethylammonium ion, respectively, as were the aluminophosphates $AlPO_4$-17 and $AlPO_4$-20. However, the presence of silica in the reaction mixture also influences structure formation. For example, the tetraethylammonium ion is a template for $AlPO_4$-5 and $AlPO_4$-18 in the aluminophosphates but produces SAPO-34, a chabazite-type structure, in the silicoaluminophosphate system. Tetrapropylammonium ion, tetrabutylammonium ion, and cyclohexylamine yield novel silicoaluminophosphate structure types which were not reported in the aluminophosphate family.

Most three-dimensional silicoaluminophosphates exhibit excellent thermal and hydrothermal stabilities. All remain crystalline after the 400–600 °C calcination necessary to remove the organic template and free the intracrystalline-void volume for adsorption or catalysis. Like aluminophosphates, most of the silicoaluminophosphates retain their structures at 1000 °C in air and at 600 °C under 20% steam.

The silicoaluminophosphate molecular sieves have intracrystalline pore volumes (H_2O) from 0.18 to 0.48 cm^3/g and adsorption pore diameters from 0.3 to 0.8 nm, spanning the range of pore volumes and pore sizes known in zeolites and in silica and aluminophosphate molecular sieves. The uniform pore dimensions defined by the crystal structure enable the use of these new materials for size- and shape-selective separations and catalysis. Properties of selected SAPO molecular sieves are given in Table I.

There are two very small pore (six-membered ring) molecular sieves, SAPO-16 and SAPO-20, which admit only small molecules such as water and ammonia. The silicoaluminophosphates that admit normal paraffins and exclude isoparaffins with eight-ring pore openings of about 4.3 Å are SAPO-17, SAPO-34, SAPO-35, SAPO-42, and SAPO-44.

SAPO-11, -31, -40, and -41 are intermediate to large in pore size. Both SAPO-11 and SAPO-41 more readily admit cyclohexane (kinetic diameter, 6.0 Å) than 2,2-dimethylpropane (kinetic diameter, 6.2 Å). SAPO-31 and SAPO-40 adsorb 2,2-dimethylpropane but exclude the larger triethylamine (kinetic diameter, 7.8 Å). The pore sizes of these structures are defined by either open 10-rings as in silicalite (6 Å) or puckered 12-rings, with 12-rings most probable for SAPO-31 and -40. The largest pore structures include SAPO-5 and SAPO-37, which have known structural analogues with circular 12-ring pore openings.

SAPO molecular sieves have tetrahedral oxide frameworks containing silicon, aluminum, and phosphorus. Mechanistically, we can consider their composition in terms of silicon substitution into hypothetical aluminophosphate frameworks. The substitution can occur via (1) silicon substitution for aluminum, (2) silicon substitution for phosphorus, or (3) simultaneous substitution of

---

(1) Breck, D. W. "Zeolite Molecular Sieves"; Wiley: New York, 1974.

(2) Flanigen, E. M.; Grose, R. W. *Adv. Chem. Ser.* **1971**, *No. 101*, 76–101.

(3) Artioli, G.; Pluth, J. J.; Smith, J. V. *Acta Crystallogr., Sect. C* **1984**, *C40*, 214–217.

(4) For example, Silicalite: Grose, R. W.; Flanigen, E. M. U.S. Pat. 4 061 724, 1977. Flanigen, E. M.; Bennett, J. M.; Grose, R. W.; Cohen, J. P.; Patton, R. L.; Kirchner, R. M.; Smith, J. V. *Nature (London)* **1978**, *271*, 512–516.

(5) (a) Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. R.; Flanigen, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 1146–1147. (b) Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. R.; Flanigen, E. M. "Intrazeolite Chemistry"; The American Chemical Society: Washington, DC, 1983; pp 79–106.

(6) Lok, B. M.; Messina, C. A.; Patton, R. L.; Gajek, R. T.; Cannan, T. R.; Flanigen, E. M. *U.S. Pat.* 4 440 871, 1984.

(7) The acronym SAPO is derived from $(Si_xAl_yP_z)O_2$. The suffix "n" denotes a specific structure type.

(8) Bennett, J. M.; Cohen, J. P.; Flanigen, E. M.; Pluth, J. J.; Smith, J. V. "Intrazeolite Chemistry"; The American Chemical Society: Washington, DC, 1983; pp 110–118.

(9) Lok, B. M.; Cannan, T. R.; Messina, C. A. *Zeolites* **1984**, *3*, 282–291.

Table I. Typical Template, Structure Type, and Adsorptive Properties of Silicoaluminophosphate Molecular Sieves

SAPO species	typical template	structure type[a]	pore size,[b] nm	ring size[c]	typical intracrystalline pore volume,[b] cm^3/g	
					O_2	H_2O
5	tri-*n*-propylamine	$AlPO_4$-5(8)	0.8	12	0.23	0.31
11	di-*n*-propylamine	$AlPO_4$-11	0.6	10 or puckered 12	0.13	0.18
16	quinuclidine	$AlPO_4$-16	0.3	6	*d*	*d*
17	quinuclidine	erionite	0.43	8	0.25	0.35
20	tetramethylammonium ion	sodalite	0.3	6	0	0.40
31	di-*n*-propylamine	$AlPO_4$-31	~0.7	10 or puckered 12	0.13	0.21
34	tetraethylammonium ion	chabazite	0.43	8	0.32	0.42
35	quinuclidine	levynite	0.43	8	0.26	0.48
37	tetrapropylammonium ion + tetramethylammonium ion	faujasite	0.8	12	0.37	0.35
40	tetrapropylammonium ion	novel	~0.7	10 or puckered 12	0.31	0.33
41	tetrabutylammonium ion	novel	0.6	10 or puckered 12	0.10	0.22
42	tetramethylammonium ion + Na	zeolite A	0.43	8	*d*	*d*
44	cyclohexylamine	novel	0.43	8	0.28	0.34

[a] Structures distinguished by their characteristic X-ray powder diffraction patterns. [b] Determined by standard McBain-Bakr gravimetric techniques after calcination (500–600 °C in air) to remove R; pore size determined from measurements on molecules of varying size (kinetic diameter from ref 1); pore volumes near saturation, O_2 at −183 °C, H_2O at ambient temperature. [c] Number of tetrahedral atoms (Si, Al, or P) in ring that controls pore size. When structure not known, estimated from adsorption measurements. [d] Sufficient adsorption data is not available for SAPO-16 and -42; pore size and ring size are estimated from structural analogues $AlPO_4$-16 and zeolite A, respectively.

Table II. *n*-Butane Cracking Results on Silicoaluminophosphates and Other Molecular Sieves

material tested[b]	k_A[a]
$AlPO_4$-5	~0.05
SAPO-5	0.2–16.1
SAPO-11	0.2–2.0
erionite[c]	4-5
SAPO-17	0.5
SAPO-31	0.1–0.9
chabazite[d]	~7
SAPO-34	0.1–3.2
SAPO-35	0.3–1.7
NH_4Y[e]	~2
SAPO-37	1.1–1.6
SAPO-40	2.4
SAPO-41	1.3
SAPO-44	1.2–2.4

[a] Typical pseudo-first-order rate constant in $cm^3/(min\ g)$. [b] Samples were precalcined in air at 500–600 °C for 1–7 h except SAPO-37 and the zeolites, which were calcined in situ. [c] Mineral zeolite erionite (Pine Valley, NV), NH_4^+ exchanged. [d] Mineral zeolite chabazite (Reese River, NV), NH_4^+ exchanged. [e] Synthetic zeolite NaY (SiO_2/Al_2O_3 = 4.8), NH_4^+ exchanged.

two silicons for one aluminum and one phosphorus. The net framework charge per framework silicon atom resulting from each substitution mode would be +1, −1, and 0, respectively. Our preliminary studies of the SAPO materials indicate that the silicon substitutes via the second and the third mechanisms. Thus some materials have anionic frameworks with a net negative charge coupled with exchangeable cations and Brønsted acid sites.

Because of the variable presence of cations and surface hydroxyl groups and the local electronegativity differences between framework Si, Al, and P, the SAPO materials exhibit a range of moderate to high hydrophilic surface properties, encompassing those shown by the aluminophosphates and by the low silica to alumina ratio zeolites, respectively.

The catalytic properties of the silicoaluminophosphate materials as demonstrated by the *n*-butane cracking values[10] (Table II) are noteworthy. The materials in general can be classified as mildly acidic, some with unique pore selectivity properties. In some structures the acidity can be varied by controlling the synthesis conditions. As shown in Table II, the materials are substantially more active than the aluminophosphates but generally less active than their zeolite analogues.

The silicoaluminophosphate materials show interesting and unique properties of potential use in adsorptive, catalytic, and ion exchange applications.

Acknowledgment. We thank S. T. Wilson for many fruitful discussions, H. Rastelli for his help in obtaining all the *n*-butane cracking k_A values, F. P. Gortsema for his help in obtaining the hydrothermal stability data, and Union Carbide Corporation for permission to publish this article.

---

(10) Rastelli, H.; Lok, B. M.; Duisman, J. A.; Earls, D. E.; Mullhaupt, J. T. *Can. J. Chem. Eng* **1982**, *60*, 44–49.

Oxymethylative Opening of Oxiranes Leading to 1,3-Diol Derivatives by Cobalt Carbonyl Catalyzed Reaction with a Hydrosilane and Carbon Monoxide[1]

Toshiaki Murai and Shinzi Kato

Department of Chemistry, Faculty of Engineering
Gifu University, Yanagido, Gifu 501-11, Japan

Shinji Murai,* Takuya Toki, Satoshi Suzuki, and
Noboru Sonoda

Department of Applied Chemistry
Faculty of Engineering, Osaka University
Suita, Osaka 565, Japan

Received July 13, 1984

Construction of the 1,3-diol system[2] is an important general problem which is often encountered in the synthesis of natural

---

(1) Previous papers: (a) Chatani N.; Furukawa, H.; Kato, T.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1984**, *106*, 430. (b) Chatani, N.; Murai, S.; Sonoda, N. *Ibid.* **1983**, *105*, 1370. (c) Murai, T.; Hatayama, Y.; Murai, S.; Sonoda, N. *Organometallics* **1983**, *2*, 1883. (d) Chatani N.; Yamasaki, Y.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1983**, *24*, 5649. (e) A review, see: Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 837.

(2) (a) Kishi, Y. *Aldrichimica Acta* **1980**, *13*, 23. (b) Masamune, S.; Choy, W. *Ibid.* **1982**, *15*, 47. (c) Minami, N.; Ko, S. S.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 1109. (d) Finan, J. M.; Kishi, Y. *Tetrahedron Lett.* **1982**, *23*, 2719. (e) Nicolaou, K. C.; Uenishi, J. *J. Chem. Soc., Chem. Commun.* **1982**, 1292. (f) Ma, P.; Martin, V. S.; Masamune, S.; Sharpless, K. B.; Viti, S. M. *J. Org. Chem.* **1982**, *47*, 1380. (g) Viti, S. M. *Tetrahedron Lett.* **1982**, *23*, 4541. (h) Heathcock, C. H.; Jarvi, E. T. *Ibid.* **1982**, *23*, 2825. (i) Heathcock, C. H.; Finkelstein, B. L. *J. Chem. Soc., Chem. Commun.* **1983**, *919*. (j) Heathcock, C. H.; Jarvi, E. T.; Rosen, T. *Tetrahedron Lett.* **1984**, *25*, 243. (k) Nakata, T.; Fukui, M.; Ohtsuka, H.; Oishi, T. *Ibid.* **1983**, *24*, 2661. (l) Roush, W. R.; Adam, M. A.; Peseckis, S. M. *Ibid.* **1983**, *24*, 1377. (m) Hirama, M.; Simizu, M.; Iwashita, M. *J. Chem. Soc., Chem. Commun.* **1983**, *599*. (n) Fleet, G. W. J.; Shing, T. K. M. *Tetrahedron Lett.* **1983**, *24*, 3657. (o) Still, W. C.; Barrish, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 2487. (p) Johnson, M. R.; Nakata, T.; Kishi, Y. *Tetrahedron Lett.* **1979**, 4343, 4347. (q) Still, W. C.; Schneider, J. A. *Ibid.* **1980**, *21*, 1035. (r) Still, W. C.; Sreekumar, C. *J. Am. Chem. Soc.* **1980**, *102*, 1201. (s) Snider, B. B.; Phillips, G. B. *J. Org. Chem.* **1983**, *48*, 2789.

0002-7863/84/1506-6093$01.50/0